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Evaluation of the Adsorption Properties of Silicalite for Potential Application to Isolating Polar Low-Molecular-Weight Organics from Drinking Water

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AN EVALUATION OF THE ADSORPTION PROPERTIES OF SILICALITE FOR POTENTIAL APPLICATION TO ISOLATING POLAR LOW-MOLECULAR-WEIGHT ORGANICS FROM DRINKING WATER

by

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68-03-2974

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16. ABSTRACT

Because of their high affinity for water, low-molecular weight polar organic compounds are difficult to isolate from drinking water as a prelude to their identification and determination. Conventional isolation techniques such as solvent extraction, adsorption, gas purging and reverse osmosis yield only low recoveries when applied to small molecules with water-like chemical and physical properties. In this work the chemical and physical properties of the adsorbent known as Silicalite were explored, the characteristics of the molecular sieve for accumulating analytes from aqueous and from gaseous streams were elucidated, techniques were developed for recovering adsorbed organic materials from the molecular sieve adsorbent, and an analytical protocol was developed for determining low-molecular weight analytes such as dichloroacetonitrile in standard samples. Accumulated organic materials were recovered from the molecular sieve by a simple, convenient and effective elution technique using a water-methanol gradient as the eluent. When adsorption and recovery procedures were combined to form an isolation protocol, it was found that compounds as diverse as phenol, acetic acid, ethyl acetate, chloroform, crotonaldehyde, propanal, acetaldehyde and butanal could be recovered from standard solutions in amounts in excess of 80% of the original concentration. When the procedure was optimized for the determination of dichloroacetonitrile, quantitative recoveries were obtained on standard samples.

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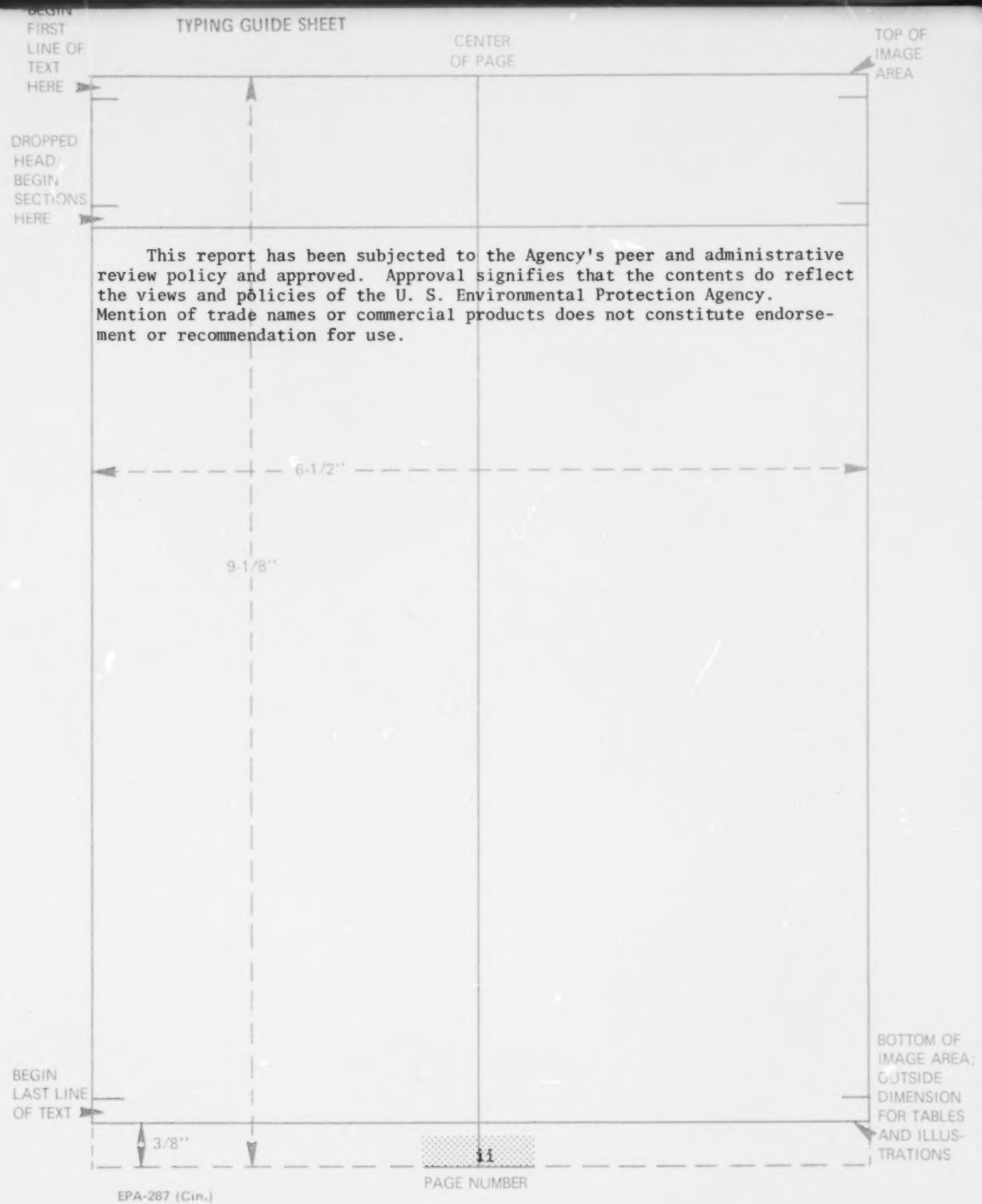
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FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our nation's population.

The complexities of environmental problems originate in the deep interdependent relationships between the various physical and biological segments of man's natural and social world. Solutions to these environmental problems require an integrated program of reserach and development using input from a number of disciplines. The Health Effects Research Laboratory conducts a coordinated environmental health research program in inhalation toxicology, genetic toxicology, neurotoxicology, developmental and experimental biology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, water pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides and other chemical pollutants. The Laboratory participates in and provides data for the development and revision of criteria documents on pollutants for which national ambient air quality and water quality standards exist or are proposed, provides, the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of environmental regulatory decisions involving the protection of the health and welfare of all U.S. inhabitants.

There is evidence that consumers are exposed to many potentially harmful chemicals in their drinking water. Most have not been effectively isolated by conventional chemical and physical techniques for measurement and identification. This report describes the potential application of an adsorption method for the isolation and measurement of low-molecular weight, highly polar, organic compounds such as aldehydes, acids, esters, ethers, ketones, nitriles and halogenated species from water.

F.G. Hueter, Ph.D.
Director
Health Effects Research Laboratory

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ABSTRACT

Isolation is the first step in the determination of many organic species in drinking water. An effective isolation technique is, therefore, essential to ascertaining whether or not potentially harmful species are present in drinking water. Conventional isolation techniques such as solvent extraction, adsorption, gas purging and reverse osmosis yield only low recoveries when applied to small molecules with water-like chemical and physical properties. Retention of organic compounds by a molecular sieve is based primarily on molecular size and studies were, therefore, performed to determine if small, water-soluble, organic species could be isolated from their aqueous matrix by adsorption on a hydrophobic molecular sieve.

In this work the chemical and physical properties of the adsorbent known as Silicalite were explored, the characteristics of the molecular sieve for accumulating analytes from aqueous and from gaseous streams were elucidated, techniques were developed for recovering adsorbed organic materials from the molecular sieve adsorbent, and an analytical protocol was developed for determining low molecular weight analytes such as dichloroacetonitrile in drinking water, although applicability has not been established.

One significant finding emerging from these studies is that Silicalite can be used to accumulate a variety of aldehydes, acids, esters, ethers, alcohols, ketones, nitriles, and halogenated species from water. Accumulated organic materials can be recovered from the molecular sieve by a simple, convenient and effective elution technique using a water-methanol gradient as the eluent. When adsorption and recovery procedures were combined to form an isolation protocol, it was found that compounds as diverse as phenol, acetic acid, ethyl acetate, chloroform, crotonaldehyde, propanal, acetaldehyde and butanal could be recovered from standard solution in amounts in excess of 80% of the original concentration. When the procedure was optimized for the determination of dichloroacetonitrile in standard samples, essentially quantitative recoveries were obtained. Tests of the protocol on finished water samples from Ames and Ottumwa, Iowa have led to inconclusive results. Compounds are isolated having gas and liquid chromatographic characteristics expected of dichloroacetonitrile, but the levels are too low to allow confirmation of identification by gas chromatography/mass spectrometry.

This report was submitted in fulfillment of Contract No. 68-03-2974 by the Ames Laboratory USDOE under sponsorship of the U.S. Environmental Protection Agency. This report covers the period from September 1980 to September 1981.

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SECTION 1

INTRODUCTION

Hundreds of different organic species have been identified in various United States drinking water supplies.[1] Most identified organic compounds are present only at ultra-trace concentrations and are not believed to pose any threat to human health or to other components of the environment. However, some materials are known to be deleterious and, thus, require that appropriate control measures be taken. Obviously before control can be accomplished, procedures must exist for characterizing and quantifying contaminants in water. Generally, techniques for determining trace constituents in drinking water are preceded by an isolation technique which serves both to concentrate the species of interest and to isolate them from the aqueous matrix. Liquid-liquid extraction, adsorption on activated carbon[2] or resins [3], inert gas purging [4], closed-loop stripping [5] and reverse osmosis [6] are techniques suitable for the isolation of most organic species from water. However, none of these are particularily effective when applied to low-molecular weight, polar organic materials. Compounds such as aldehydes, ketones, nitriles and alcohols are too water-like in their chemical and physical properties for effective isolation by conventional procedures.

A hydrophobic molecular sieve recently was introduced by Union Carbide [7]. This material, known as Silicalite, is a unique, crystalline, hydrophobic molecular sieve possessing six Angstrom diameter pores which occupy 19% of the bed volume. It has been suggested that Silicalite could be used in the treatment of wastewater for the removal of species such as benzene, phenol, propanol and hexane.[8] It has been demonstrated that Silicalite is effective for removing chloroform from drinking water [9] and for the recovery of ethanol from fermentation beer.[10]

Based on the ability of Silicalite to adsorb polar as well as non-polar low-molecular weight organic species from aqueous solutions, studies were performed to determine if this adsorbent could be used to isolate small, polar organic substances from drinking water as a prelude to their determinations. Details of the studies performed and the results obtained comprise the remainder of this report.

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SECTION 2

CONCLUSIONS

This work has shown that Silicalite molecular sieve is effective for accumulating various aldehydes, alcohols, nitriles, organic acids, esters, ketones, ethers, and chlorinated hydrocarbons from water. Using distribution coefficients as a measure of the relative affinity of Silicalite for organic species indicates that slightly polar compounds such as aldehydes and esters are better retained than more polar substances such as nitriles and alcohols an that organic acids and one or two carbon alcohols are only poorly retained. These findings are reasonable because highly polar materials have a great affinity for water. It was also found that large molecules such as octanal and decanal are less well retained than are smaller aldehydes such as propanal and pentanal. This finding is also reasonable because the larger molecules would have to unfold and assume a linear conformation to enter the pore structure of the molecular sieve.

Thermal elution, microwave elution, adsorbent dissolution and solvent elution were all evaluated as potential means for isolating accumulated species from the molecular sieve. It was found that elution with methanol provided the simplest and most convenient general procedure for recovering adsorbed analytes from Silicalite. Other techniques were applicable to a narrow range of analytes, led to decomposition of analytes, or were excessively complicated. Elution with acetonitrile is more effective for the recovery of higher molecular weight aldehydes, however, than was elution with methanol.

An analytical protocol was optimized for determining dichloroacetonitrile in standard samples that yielded excellent recoveries when applied to standard samples. Using this procedure dichloroacetonitrile was apparently detected in water from Ames and from Ottumwa, Iowa. However, the levels detected were below limits which can be confirmed by gas chromatography/mas spectrometry. Thus, it is not known if dichloroacetonitrile is actually present in these water supplies or if some other unidentified constituent of the water interferes with the determination of dichloroacetonitrile or if in fact, the protocol can be successfully applied to real samples. Modifications of the protocol developed for dichloroacetonitrile have proven suitable for the isolation of chloroform, ethyl acetate, crotonaldehyde, propanal, acetaldehyde, and butanal from standard samples, but was not verified on real samples.

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SECTION 3

RECOMMENDATIONS

The present work has been successful in elucidating the basic properties of Silicalite and has also led to the development of what appear to be viable analytical protocols for determining low-molecular weight organic species such as dichloroacetonitrile in drinking water. However, as is often the case with research, this study has provided more questions than answers.

Continued development of this adsorbent as an analytical agent would undoubtedly lead to the development of an entire family of methods for determining low-molecular weight organic compounds in water. Continued development should proceed and application to real samples demonstrated.

In the course of elucidating the basic properties of Silicalite it has been shown that this molecular sieve is an excellent adsorbent for a diverse assortment of organic and inorganic gases. Continued research could lead to the development of improved techniques for sampling gaseous streams such as ambient air and gaseous effluents. This possibility should be explored further.

In a closely related application, there is the significant probability that Silicalite could be used in inert gas purging or closed-loop stripping procedures either as a replacemment for currently used adsorbents or in combination with them. In such an application it is expected that Silicalite would trap materials that are not retained on conventional adsorbents. An evaluation of Silicalite for this application is strongly recommended.

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SECTION 4

CHEMICAL AND PHYSICAL PROPERTIES OF SILICALITE

MOLECULAR SIEVE ADSORBENTS

Molecular sieves are porous solid adsorbents. Retention on a molecular sieve is dependent on molecular size. In general the pores of a molecular sieve have consistent diameters, and the diameters are within the range of the sizes of molecules in solution. Molecules having diameters larger than the pore diameter cannot enter the pore structure and cannot be retained. Molecules having diameters far smaller than the pore diameter of the molecular sieve can enter the pore structure, but are generally only poorly retained because they can also leave the pore structure readily. Molecules having diameters only slightly smaller than the pore diameter of the molecular sieve can also enter the pore structure, but once in the pore structure, movement is restricted and such compounds are well retained.

The simplified description above ignores interactions between the molecular sieve and compounds. Obviously interactions do occur. Conventional molecular sieves are crystalline alumina-silicates. They contain metal ions and hydroxyl groups as elements of the crystal structure, and these make the molecular sieves polar adsorbents. As polar adsorbents for small molecules, alumina-silicate molecular sieves are widely used for removing water from non-polar solvents and from gaseous streams.

SILICALITE MOLECULAR SIEVE

Four years ago the Linde Division of Union Carbide developed a unique molecular sieve now known as Silicalite[8]. In contrast to conventional hydrophillic molecular sieves, Silicalite is hydrophobic, and the hydrophobic character is what makes Silicalite unique. Silicalite can be used to accumulate organic species from aqueous solutions, whereas conventional molecular sieves are used to accumulate water from organic solvents.

Silicalite is a polymorph of silica with a special crystal structure. It is tetrahedral framework with a large fraction of five-membered rings composed of silicon-oxygen tetrahedra. The structure has intersecting channels defined by ten-membered rings of oxygen in all directions. The precursor state of Silicalite is formed by the hydrothermal crystalliztion of silica and alkyl ammonium hydroxides. The silica forms clathrates around the alkyl ammonium ions. To produce the open pore structure, the precursor is calcined in air to drive off alkyl ammonium hydroxide. The resulting channels are six Angstroms in diameter and occupy 33% of the

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total crystal volume. The crystalline Silicalite formed by this process has the empirical formula SiO_2, and is in the form of particles approximately 20 x 20 x 70 microns. In this report this material will be referred to as unbound Silicalite. Various alumina, alumina-silicate, and silicate clays have been used as binders to form larger particles of Silicalite. Materials containing these binders will be referred to as bound Silicalite or simply as Silicalite.

Silicalite is stable at high temperatures. Decomposition begins only at temperatures greater than 1100° C, and at 1350° C Silicalite reverts to amorphous silica. It is stable in the presence of solvents and most corrosives including strong acids and oxidizing agents. It is slowly decomposed by strong bases and dissolves in hydrofluoric acid. Granules of bound Silicalite are brittle and can be broken into a powder during handling.

Materials accumulated by Silicalite must be smaller than six Angstroms in diameter or assume a conformation smaller than that size. Water molecules are small enough to be adsorbed. However, in the liquid state each water molecule is hydrogen bonded to adjacent water molecules to form groups containing on the average 10 to 12 molecules. This grouping of water molecules is larger than the pore diameter of Silicalite and would have to be dissociated in order to enter the pore structure. The energy of adsorption of water is less than the energy of hydrogen bonding between water molecules. Thus, Silicalite is hydrophobic.

Silicalite will adsorb small organic molecules from aqueous solutions. In the initial announcements of the discovery of Silicalite it was suggested that it might have utility for the treatment of wastewater for the removal of small organic species such as phenol, benzene, propanol, and hexane[8]. It has since been shown that Silicalite can also be used to remove the trace levels of chloroform produced in drinking water as the result of reactions between the chlorine disinfectants and organic materials.[9] In this potential application the capacity of Silicalite is far greater than that of alternative adsorbents such as activated carbons or synthetic resins, and Silicalite can be regenerated far more readily. It is also competitive in cost with other adsorbents. However, Silicalite will not adsorb many of the species believed to be precursors of chloroform in drinking water. Other potential applications suggested for Silicalite have been for the recovery of ethanol from fermentation beer.[10] With this application, adsorption offers a potentially less costly, more energy efficient alternative to distillation procedures currently used for producing ethanolic fuels.

SECTION 5

ADSORPTION OF ANALYTES FROM WATER

The primary requirement of an adsorbent to be used for isolating a material from water is, of course, that it be able to take up the compound of interest. Studies were performed to determine the characteristics of compounds which could be accumulated by Silicalite from water.

AQUEOUS PHASE DISTRIBUTION COEFFICIENTS

Experimental Procedure

Solutions were prepared containing 10 mg/L of selected analytes in deionized, organic-free water. Ten mL aliquots of these solutions were equilibrated with known amounts of bound Silicalite. The amount of Silicalite used varied from 0.1 to 0.5 g depending on the analyte under investigation. The Silicalite was a material designated as LZ-115 by Union Carbide. This material is believed to contain 10% by weight of an aluminasilicate clay which serves as a binder. Equilibration consisted of shaking the solution with Silicalite for a period of one hour on a motorized shaking bed. After equilibration, an aliquot of the water was removed, it was separated from the Silicalite by filtration, and the concentration of analyte in the water determined. Organic acids were determined by titration with sodium hydroxide solutions using phenolphthalein indicator. Other analytes were determined by gas chromatography using a Tracor Model 560 equipped with flame ionization detectors.

Measurements and Calculations

From determinations of the concentration of analyte in the aqueous phase and the amount originally added, the amount accumulated by the Silicalite can be calculated by difference. The distribution coefficient, D_g, is then calculated using the expression:

$$D_g = \frac{(A_s)(\text{Vol, ml})}{(A_w)(\text{Wt, gm})}$$

In this expression A_s is the amount of analyte on the Silicalite, A_w is the amount in the water, Wt is the weight of Silicalite, and Vol is the volume of water.

Experimental Results

As can be seen in Table 1, most compounds are well taken up by Silicalite.

TABLE 1. DISTRIBUTION COEFFICIENTS BETWEEN SILICALITE AND WATER

Compound	D_g	Compound	D_g
acetic acid	72	methyl formate	2090
pyruvic acid	29	ethyl acetate	4970
trichloroacetic acid	47	acetaldehyde	100
ethanol	65	acrolein	580
propanol	250	crotonaldehyde	1340
phenol	170	furfural	1100
bis-(2-chloroethyl)ether	270	propanal	1350
acetone	270	butanal	88 (>2000)*
isophorone	1	pentanal	2800
methyl, isobutyl ketone	2770	hexanal	940
acetonitrile	150	heptanal	440
dichloroacetonitrile	>600	octanal	570
chloroform	1230	nonanal	130
acrylonitrile	220	decanal	240
		2-chloroacetaldehyde	23

*2000 based on column equilibrium

Although most compounds tested would be considered as at least relatively polar, there is a trend that the least polar of these have higher distribution coefficients than do the most polar. For example, esters have a greater affinity for Silicalite than do acids. The effect of molecular size upon accumulation is best seen with the aldehyde series. Pentanal has a distribution coefficient of 2800. Lower molecular weight aldehydes have lower distribution coefficients in part because they are more polar and thus have a greater affinity for water and in part because with their smaller size they are not restricted in movement once in the pore structure and can, thus, leave the pore structure more readily. The larger aldehydes must assume a linear, strained conformation to enter the pore structure.

Only a minimal value was obtained for the distribution coefficient for dichloroacetonitrile because of difficulties in measuring the low concentrations of this species remaining in water after equilibration. However, the value obtained does indicate that dichloroacetonitrile is efficiently accumulated by Silicalite. This compound is of special interest because it is a potential carcinogen, it is believed to be produced in drinking water during chlorination, and it may be a precursor for chloroform.[11]

The values obtained for a distribution coefficient for butanal are of

great concern simply because they are inconsistent with those obtained from companion studies for propanal and pentanal. The value of 88 was obtained and confirmed by replicate determinations. Retention of butanal on Silicalite-loaded columns indicates the distribution coefficient is in excess of 2000. Apparently some, as yet undetected, event happens during equilibrium accumulation experiments which prevents the accumulation of butanal or, for some unexplained reasons, determinations of butanal in water remaining after equilibration have a large positive interference.

Distribution coefficients can be used as a rough guide in predicting whether or not a compound can be accumulated from water. Because the values in Table 1 were obtained at a single analyte concentration and were obtained under equilibrium conditions, they will not accurately predict the recovery of a given analyte accumulated under dynamic conditions on a column and at different concentrations. However, trends can be predicted. From these data it can be predicted that acetic acid, for example, could be accumulated efficiently only when small volumes of water were processed and while ethyl acetate, for example, could be efficiently accumulated from from far larger volumes of water.

ADSORBENT CAPACITY

Experimental Procedures

Solutions were pumped through a 250 mm x 4 mm i.d. column packed with bound Silicalite using a Milton Roy Duplex pump. For most analytes the concentration was continuously monitored in the effluent using a Tracor Model 970A variable wavelength detector. Fractions of effluents containing ethanol and chloroform were collected and levels determined by gas chromatography using a Varian Series 1400 gas chromatograph. In all cases the data were used to construct a breakthrough curve in which the fraction of the influent concentration of analyte found in the effluent is plotted against the amount of analyte passed through the column.

From the breakthrough curves the amount of analyte accumulated per gram of Silicalite was calculated for points where the analyte concentration in the effluent was 1%, 10% and 50% of the influent concentration.

Experimental Results

In analytical applications the capacity of an adsorbent is rarely exceeded. The values for 1% and 10% breakthrough do, however, provide a measure of the amount of material that can be accumulated on a column while retaining 99% and 90% of the analyte, respectively. The value for 50% breakthrough is of more interest if the adsorbent were used in the treatment of water for removal of the species.

As shown in Table 2, with the exception of acetic acid, all compounds tested possessed 1% breakthrough capacities in excess of 1 mg/g. This indicates that in the very prevalent situation in which a milligram is required for determinations, that this amount could be recovered with 99%

efficiency on an adsorbent bed containing one gram of Silicalite.

TABLE 2. BREAKTHROUGH CAPACITIES FOR COMPOUNDS IN WATER

Compound	Capacity in mg/g at given % breakthrough* 1%	10%	50%
acetic acid	0.2	3	9
phenol	18	130	151
ethanol	120	high	high (<240)
acrolein	22	29	high (< 220)
crotonaldehyde	7	12	27
propanal	63	83	high (< 240)
butanal	42	55	81
pentanal	36	high	high (<240)
furfural	24	42	58
ethyl acetate	90	100	110
acetone	20	29	52
acetonitrile	150	high	high (<240)
chloroform	1	3	10

* 10% or 50% breakthrough did not occur with some compounds before the run was terminated. 10% and 50% breakthrough capacities for these compounds are higher than the 1% capacity.

In actual practice, larger beds of adsorbent would be required than are indicated by breakthrough capacity because a minimum bed depth is required for contact and this minimum is dependent on factors such as flow rate, analyte concentration and particle size.

SECTION 6

GAS PHASE ADSORPTION ON SILICALITE

Most data obtained in this section were obtained during work on other, separately funded projects. They are included because they have direct bearing on the adsorptive properties of Silicalite and thus relate to the present work.

DISTRIBUTION COEFFICIENTS

Experimental Procedures

Studies were performed using a Gow Mac Model 550 gas chromatograph equipped with thermal conductivity detectors. Columns were 4 mm i.d. x 200 mm packed with bound and non-bound Silicalite. High purity helium was used as a carrier gas. Samples of pure compounds were injected and retention time measured. The retention time of 2,2,4-trimethylpentane was used to measure the retention time of an unretained species. Distribution coefficients were calculated using the expression:

$$D_g = \frac{(RT)(F) - DV}{Wt}$$

RT is the retention time of the compound of interest, F is the flow rate of the carrier gas in mL/min, DV is the dead volume in mL, and Wt is the weight of Silicalite in the column.

Experimental Results

Gas phase distribution coefficients for selected compounds are listed in Table 3. As would be expected, the distribution coefficients decrease as temperature increases. For some compounds such as ethyl acetate the distribution coefficients are very large even at temperatures as high as 250° C. This would indicate that recovery of such compounds from Silicalite by thermal elution would be accomplished with great difficulty. It is also evident that the distribution coefficients for gases varies over a significant range.

TABLE 3. GAS PHASE DISTRIBUTION COEFFICIENTS ON UNBOUND SILICALITE

Compound	Distribution Coefficient at Given Temperature				
	250°C	200°C	150°C	100°C	50°C
methane	2	2	4	7	24
ethane	4	8	18	46	300
propane	9	22	62	220	
pentane	51	200			
hexane	120	>400			
heptane	310	>400			
ethylene	4	6			
cyclopropane	8	23	56	160	
cyclohexane	110	>400			
cyclohexene	79	310			
2-methylpentane	86	380			
2,2,4-trimethylpentane	0	1	2	6	
benzene	1	2	4	11	
methanol	12	60	100		
ethanol	26	100	200		
propanol	40	100			
isobutanol	50	400			
undecanol	90	>400			
acetaldehyde	30	50	170		
propanal	20	40	130		
butanal	60	140			
acetic acid	26	260			
lactic acid	13	62			
pyruvic acid	5	12	27	62	
acetone	50	200			
isophorone	5	26			
methyl formate	40	88			
ethyl acetate	100	>400			
bromobenzene	140	>400			
carbon tetrachloride	55	280			
chloroform	40	90	>400		
water	7	16	19	74	
air	1	2	3	3	9
oxygen	2	3	3	4	9
nitrogen	1	2	3	3	9
nitrous oxide	4	2	3	20	
carbon monoxide	2	2	3	4	11
carbon dioxide	3	5	9	16	77
sulfur dioxide	12	23	74	130	>1000

A comparison of gas phase distribution coefficients obtained at 250° C using bound and unbound Silicalite is given in Table 4.

TABLE 4. DISTRIBUTION COEFFICIENTS AT 250° C ON SILICALITE

Compound	D_g Bound	Unbound	Compound	Bound	Unbound
acetic acid	25	26	benzene	0	1
pyruvic acid	2	5	bromobenzene	47	140
trichloroacetic acid	2	2	methane	1	2
ethanol	70	26	ethane	2	4
propanol	100	40	propane	4	9
phenol	24	28	butane	6	16
formaldehyde	5	5	pentane	24	51
acetaldehyde	16	30	hexane	53	120
propanal	50	20	ethylene	2	4
butanal	70	60	cyclopropane	4	8
acrolein	60	46	acetylene	2	4
crotonaldehyde	45	61	neopentane	0	39
furfural	170	290	dichloromethane	20	40
2-chloroacetaldehyde	> 780	300	chloroform	23	40
methyl formate	20	40	carbon tetrachloride	2	55
ethyl acetate	69	100	1,2-dichloroethane	60	70
acetone	34	50	tetrachloroethylene	4	30
isophorone	16	5	1-chlorododecane	25	33
methyl, isobutyl ketone	100	200	oxygen	1	2
acetonitrile	48	64	nitrogen	0	1
acrylonitrile	82	89	hydrogen sulfide	6	20
dichloroacetonitrile	63	85	hydrogen chloride	30	20
diethyl ether	90	80	nitrous oxide	2	4
bis(2-chloroethyl) ether	143	138	carbon monoxide	1	2
			sulfur dioxide	7	12
			ammonia	30	40

The most significant point of these data is that the binder does indeed affect the properties of Silicalite as an adsorbent. The most significant effect is seen with compounds such as neopentane, carbon tetrachloride and tetrachlorethylene. In each of the cases the unbound Silicalite had a far greater affinity for the analyte than did the material containing a binder. Each of these analytes has a molecular diameter approximately the same as the pore diameter of Silicalite and, thus, it is rationalized that the binder was restricting access to the pores. With ethanol, propanol, propanal, 2 chloroacetaldehyde, isophorone, and hydrogen chloride the material containing a binder had a greater affinity for the analytes than did the unbound Silicalite. It is assumed that the binder interacts with the analyte in some manner in these instances. In only relatively few cases was there no significant difference between the bound and unbound Silicalite.

Silicalite is currently supplied in experimental quantitates by Union Carbide. When commercial production commences the material may or may not contain a binder formulation similar to those used in experimental formulations. Because the binder does have a significant effect on adsorptive properties of Silicalite, it is important to note that essentially all the experiments reported on in this report utilized a material designated as LZ-115 and containing 10% by weight of an alumina-silicalite clay binder.

CAPACITY OF SILICALITE FOR GASES

Experimental Procedures

Altex glass columns, 12 mm i.d. x 250 mm. were packed with 10 g of Silicalite. Helium gas was passed through until a constant weight was obtained. A test gas was then passed through the bed at a nominal flow rate of 35 mL/min until the column reached a constant weight. The difference in the initial and final weight of the bed was the amount of gas adsorbed.

Experimental Results

When the capacity of Silicalite is expressed in terms of mg/g or mL/g there are wide variations in the capacity among the various gases tested. However, if it is assumed that gases condense upon adsorption, the variations are considerably smaller. It is evident from the data in Table 5 that gases are adsorbed in some condensed state merely because the volume of gas accumulated generally exceeds the total pore volume, which is 0.19 mL/g, and the total bed volume, which is approximately 2 mL/g.

TABLE 5. SILICALITE CAPACITY FOR GASES VS. HELIUM AT 25° C

Gas	Capacity/g			Gas	Capacity/g		
	mg	mL_g	mL_l		mg	mg_g	mL_l
methane	6	8	.01	nitrogen	8	6	.01
ethane	53	40	.08	oxygen	8	6	.01
propane	77	39	.12	carbon monoxide	13	10	.02
butane	98	38	.14	carbon dioxide	70	36	.06
ethylene	40	32	.06	sulfur dioxide	190	67	.13
propylene	59	32	.09	ammonia	70	92	.09
1-butylene	110	44	.16	hydrogen sulfide	80	53	.08
cyclopropane	99	53	.15	carbonyl sulfide	120	45	.10
isobutane	102	39	.15	dichlorodifluoro-methane	180	33	.12
dimethyl ether	107	52	.15				
dimethyl mercaptan	145	68	.17	chlorotrifluoro-methane	152	33	.10
neopentane	93	29	.14				

mg = observed weight of gas accumulated, mL_g = calculated volume of gas accumulated, mL_l = calculated volume of liquid accumulated.

SECTION 7

DESORPTION OF MATERIALS FROM SILICALITE

Adsorption of a material is of little value in an analytical procedure unless the adsorbed material can be recovered from the adsorbent. During the course of this study considerable effort was directed towards the development of a technique for recovering accumulated analytes from Silicalite. The solvent elution procedure described below provides a convenient and effective means for recovery of those analytes tested in this work. However, because Silicalite may well be used for other materials, alternative desorption techniques are also described.

SOLVENT ELUTION

Elution of analytes from Silicalite is basically a very simple procedure. Details of the technique are, however, important to adhere to, to avoid disappointing results. Most analytes studied can be recovered using a gradient elution going from 100% deionized, organic free, deaerated water to 100% methanol in fifteen minutes at a flow rate of one mL/min (for a 4.6 mm i.d. x 150 mm column). During gradient elution most analytes are completely retained until the methanol concentration reaches 100%. Decanal is not eluted by this procedure but is recovered using an essentially identical procedure in which acetonitrile is substituted for methanol.

Despite the fact that analytes are not eluted until pure methanol enters the column, the use of a gradient is critical. The pores of Silicalite are initially filled with air. During adsorption of analytes from water some of this air is replaced by the materials adsorbed. However, even at the end of a typical accumulation procedure the bed will still contain about 5 mL of adsorbed air per gram of Silicalite. This air is displaced by the elution solvent. If a gradient elution is used, the air will be displaced slowly and most of it will dissolve in the deaerated water which comprises most of the initial elution solvent. If the bed was eluted directly with methanol or acetonitrile, the adsorbed air would be displaced rapidly (with evolution of heat) and would create pockets in the bed. The elution solvent would channel around these pockets and miss portions of the Silicalite. Thus, gradient elution provides a means of desorbing accumulated analytes without disrupting the bed.

OTHER DESORPTION TECHNIQUES

Soxhlet Extraction

Soxhlet extraction was attempted with a variety of solvents and mixed solvents. Difficulty was encountered in finding a solvent which was effective and not considerably less volatile than the analytes studied. However, acceptable recoveries could be obtained with several solvents. This approach was abandoned in favor of the simpler elution technique.

High Pressure Soxhlet Extraction

High pressure Soxhlet extraction (12) differs from normal Soxhlet extraction in that the entire extraction device is encased in a pressure bomb and the solvents used are ones which would be gases at normal pressures. The advantages of this technique are that some unique solvents can be used such as Freons™, propane, butane, ammonia, sulfur dioxide, dimethyl ether, and carbon dioxide, and that when the pressure is released from the bomb the solvent evaporates at low temperatures leaving behind a solvent-free sample. A major disadvantage of this technique is that the extraction takes place within a stainless steel bomb and there is no way to observe whether or not reflux has commenced or to determine the number of extraction cycles that occur.

Initial work with this technique indicated that dimethyl ether would yield reasonable recoveries of analytes from Silicalite. Carbon dioxide and propane also appeared to have some utility. This development was halted because of the development of an effective elution technique.

Adsorbent Dissolution

In previous work it was demonstrated that irreversibly adsorbed materials could be recovered from Florisil by dissolving the adsorbent in hydrofluoric acid and extracting the analytes from the acid.(13) A similar technique has been developed for determining phenol adsorbed on fly ash.(14) In the present work it was found that Silicalite will dissolve readily in hydrofluoric acid and that some relatively inert materials can be subsequently extracted from the acid.

Microwave Desorption

Silicalite does not adsorb microwaves. An attempt was made to desorb organic species from Silicalite by irradiating a bed placed within the oven of a home-type microwave oven. The process worked well for the recovery of alcohols but did not work for other analytes. It was not considered practical to pursue these investigations with microwave equipment capable of emitting other frequencies of radiation because of the excessive cost of such equipment.

Thermal Desorption

Thermal elution of adsorbed analytes directly into the injection area of a gas chromatograph was initially the method of choice for recovering analytes from Silicalite. This procedure would eliminate much of the handling of samples, it could be largely automated, and because Silicalite is stable up to temperatures in excess of 1100° C, blank interferences could be eliminated by pretreatment of the adsorbent.

It was found that thermal elution could be used for relatively stable compounds such as chloroform. However, most of the analytes of interest required high temperatures for elution from the Silicalite and they appeared to decompose at those temperatures. Other analytes appeared to decompose at even relatively low temperatures. Thus, when attempts were made to recover dichloroacetonitrile, for example, as many as four different fragments would be detected in the profile.

It is still believed that by proper selection of the carrier gas and rigid control of temperatures that thermal elution could be applied to a large number of species accumulated from drinking water on Silicalite. Unfortunately, the conditions have not yet been discovered.

SECTION 8

DETERMINATION OF LOW MOLECULAR WEIGHT ORGANIC SPECIES IN WATER

EXPERIMENTAL

Reagents and Chemicals

Solvents used with high purity, "distilled-in-glass" quality were obtained from Burdick and Jackson Laboratories, Muskegon, Michigan. Deionized water was further purified by passage through a Milli-Q water purification system. Water was then deaerated by purging with helium. Helium purge was maintained continuously to prevent readsorption of air or contaminants from the air. All reagents used were of 97% or higher purity except dichloroacetonitrile (90%).

Equipment and Apparatus

A Spectra Physics Model SP8000 liquid chromatograph was used for both accumulation of organic materials from water and their subsequent elution from Silicalite-loaded columns. This instrument is equipped with a ternary gradient capability, a 254 nm UV detector, and a Tracor Model 970A variable wavelength UV detector. Gas chromatographic determinations were performed using a Tracor Model 560 equipped with dual flame ionization detectors and a Tracor Model 550 equipped with an electron capture detector.

Adsorption Columns

To prepare an adsorption column pack a 4.6 mm i.d. x 140 mm stainless steel column with 80 to 100 mesh Silicalite slurried in water at a pressure of 5000 p.s.i. Wash the packed column with 30 mL of methanol followed by 30 mL of organic-free water.

Adsorption of Dichloroacetonitrile from Water

Connect the Silicalite column to an HPLC system in series with a 4.6 mm x 250 mm Lichrosorb RP-8 column (Jones Chromatography, Columbus, Ohio) as shown in Figure 1. Pump 200 mL of sample through, bypassing the Silicalite and RP-8 columns, to flush the system. Pump an appropriate volume of the sample through the Silicalite column bypassing the RP-8 column. During this accumulation step the flow rate is maintained at four mL/min, the temperature at 25° C, and the pressure is generally about 1000 p.s.i. The volume of sample pumped through the column is dependent

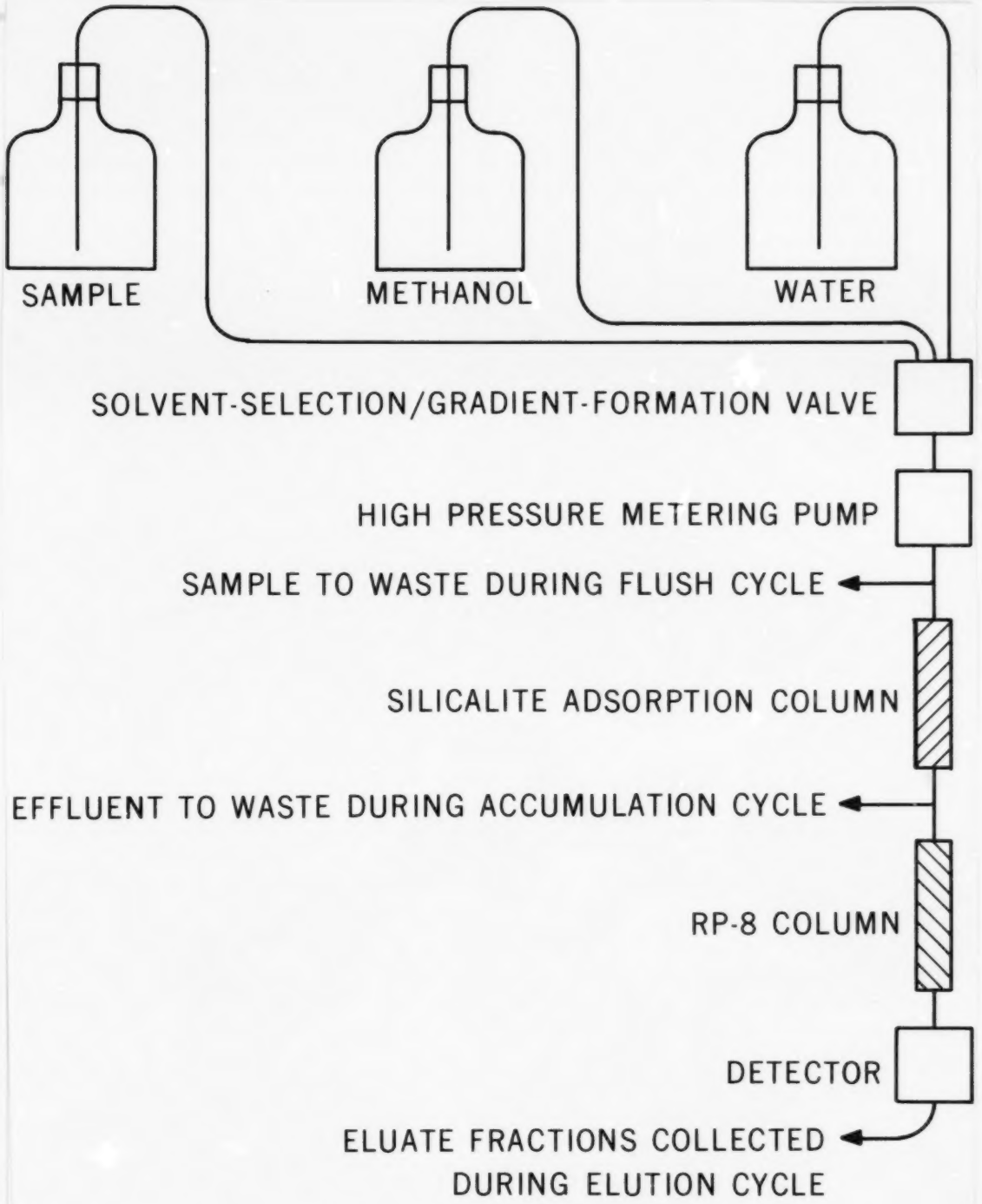

Figure 1. Experimental Apparatus

on the sensitivity of the analytical detection method used and the level of analyte present in the sample.

Recovery of Dichloroacetonitrile from Silicalite

When accumulation is completed, attach the RP-8 column in series with the Silicalite column. The RP-8 serves to partially separate eluted compounds. Begin elution with a gradient going from 100% water to 100% methanol in 15 minutes. Temperature is maintained at 25° C and flow rate is reduced to one mL/min during elution. The back pressure will rise to about 2000 p.s.i. When the elution solvent reaches its final composition, maintain that composition.

Collect the fraction of the eluent eluting between 18 and 28 minutes after the start of elution. This fraction will contain the dichloroacetonitrile.

Determination of Dichloroacetonitrile

For samples containing greater than 0.1 mg of dichloroacetonitrile, the concentrations can be determined by gas chromatography using a flame ionization detector-equipped instrument. Two µL of sample is injected at an initial temperature of 150° C. This temperature is maintained for two minutes and then increased to 250° C at a linear rate of 15°C/min and held at that temperature. A 2 mm i.d. x 1.6 M glass column packed with Porapack Q is used.

For a sample containing less than 0.1 mg of dichloroacetonitrile, an electron capture detector-equipped instrument is used. An isothermal temperature of 230° C is maintained and the column is the same.

For capillary GC/MS determinations the methanol eluent is diluted to 100 mL with water and extracted with 5 mL of pentane or 5 mL of dichloromethane. A 30 M SE-54 WCOT fused silica column is used. Sensitivity is comparable to that obtained using the flame ionization detector-equipped instrument.

EXPERIMENTAL RESULTS

Recovery of Dichloroacetonitrile

An initial concern was whether or not dichloroacetonitrile could be recovered from Silicalite quantitatively. Columns were loaded with 2.5 mg of dichloroacetonitrile by adding concentrated solutions to the column and eluting with methanol. It was found that recoveries greater than 99% could be attained. Examination of the recovered materials by GC/MS confirmed that the recovered material was dichloroacetonitrile and not an artifact or degradation product.

The ability to elute small volumes of dichloroacetonitrile was confirmed in studies in which 100, 10 and 1 µg amounts of the analyte were

loaded on a column and eluted with a methanol-water gradient. As is shown in Table 6, essentially quantitative recovery was obtained at all levels.

TABLE 6. RECOVERY OF DICHLOROACETONITRILE FROM SILICALITE

Amount Loaded, µg	% Recovered	RSD
100	96	4
10	99	1
1	98	2

The recommended procedure was further tested by loading various volumes of water containing various concentrations of dichloroacetonitrile on Silicalite, eluting, and determining recoveries. As is shown in Table 7, near quantitative recoveries were obtained at concentrations ranging from 10 to 100 µg/L using sample volumes ranging from 100 to 780 mL.

TABLE 7. RECOVERY OF DICHLOROACETONITRILE FROM STANDARDS

Concentration added, µg/L	Sample Volume, mL	Amount, µg, of Dichloroacetonitrile	% Recovery
100	100	10	102
100	500	50	98
100	780	78	105
10	100	1	105
10	780	7.8	98

Determination of Dichloroacetonitrile in Drinking Water

Application of the recommended procedure to drinking water from Ames, Iowa indicated a concentration of 0.1 µg/L. The amount found is below the detection limit of the GC/MS system and the identity of dichloroacetonitrile cannot be confirmed.

The recommended procedure was also applied to samples from Ottumwa, Iowa. In this instance samples of raw water, finished water from the treatment plant, and finished water from the distribution system were taken. No dichloroacetonitrile was detected in the raw water. Peaks having retention times corresponding to the retention time of dichloroacetonitrile were present in chromatograms of the finished and distribution system water. The identities of these peaks could not be determined by GC/MS. Previous work has shown that dichloroacetonitrile decomposes rapidly at basic pH levels and Ottumwa water has a pH of about 9.

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Thus, it is unlikely that these peaks are due to dichloroacetonitrile.

At the present time the status of application of the recommended procedure to "real" water samples has not been established. However, indications are that the procedure should work if a water supply is located containing detectable amounts of dichloroacetonitrile.

APPLICATION OF THE RECOMMENDED PROCEDURE TO OTHER ANALYTES

The recommended procedure was applied to samples prepared to contain chloroform, phenol, ethyl acetate, crotonaldehyde, propanal, acetaldehyde and butanal. In all cases recoveries in excess of 80% were obtained. It was also found that decanal could not be recovered using this procedure but could be recovered if acetonitrile was used in place of methanol as the elution solvent. Application of the recommended procedure has not been tested on real samples for any analytes.

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